Cr$_2$O$_3$ is antiferromagnetic:
Néel temperature
$T_N = 307.6$ K
Two 180° domains (+/−),

symmetry $T > T_N$: 
$D_{3d} = \overline{3}m$ with: 
inversion $I$
time reversal $T$
and thus $TI$

symmetry $T < T_N$: 
$D_{3d}(D_3) = \overline{3}m$ with: 
inversion $I$
but still $TI$

Symmetry operations:

$\overline{3}$m: 1, 1, 3(2$_\perp$), 3(2$_\perp$), ±$3_z$, ±$\overline{3}_z$
1, 1, 3(2$_\perp$), 3(2$_\perp$), ±$3_z$, ±$\overline{3}_z$

$\bar{3}$m: 1, 3(2$_\perp$), ±$3_z$, 1, 3(2$_\perp$), ±$\overline{3}_z$
Temperature Dependence of SHG in Cr$_2$O$_3$
Antiferromagnetic 180° Domains in Cr$_2$O$_3$

Domain topography with SHG:
Exposure time: ~ 1 min
Resolution: ~ 1-10 µm
Photon energy here: 2.1 eV

Magnetic Symmetry of Hexagonal $RMnO_3$

$RMnO_3$: A highly correlated and ordered system

- **Paraelectric $\rightarrow$ Ferroelectric**
  (PEL - FEL): $T_C = 570 - 990$ K
  Two 180° domains with $\pm P_z$

- **Para- $\rightarrow$ Antiferromagnetic**
  (PM - AFM): $T_N = 70 - 130$ K
  8 frustrated triangle structures

- Multiferroic/hexagonal for $R =$ Sc,Y,In,Dy,Ho,Er,Tm,Yb,Lu

- Additional rare-earth order at
  $\approx 5$ K for Dy, Ho, Er, Tm, Yb
Second-Harmonic Spectroscopy of YMnO$_3$

\[ \chi_{zyy} \quad \text{YMnO}_3 \quad T = 6 \text{ K} \]

- 3$d^3$ transitions of 5-fold coordinated Mn$^{3+}$ ion
- Transitions of magnetic and nonmagnetic origin
- Magnetic structure: P$6_3$cm
Domains in YMnO$_3$ by SHG:

- Reversal of the ferroelectric (FEL) order couples to the reversal of the antiferromagnetic (AFM) order

- Coexistence of "free" and "clamped" antiferromagnetic walls

- Strong magnetoelectric coupling at the walls, but no coupling in the bulk

- Multiferroics not a mandatory source of strong magnetoelectric effects!

Coupling of Magnetic and Electric Domain Walls

- **AFM wall** carries magnetization $\mathbf{M}$
- **FEL wall** induces strain $\sigma$
- **Width of walls:**
  - AFM – $O[10^3]$ unit cells: small in-plane anisotropy
  - FEL – $O[10^0]$ unit cells: large uniaxial anisotropy

Piezomagnetic effect $H_{pm} = q_{ijk} M_i \sigma_{jk}$ as higher-order magnetoelectric effect

Coupling of antiferromagnetic to ferroelectric wall reduces free energy!

Magnetic Structure and Selection Rules for SHG

At least 8 different structures with different symmetries and SHG contributions

\[ P_i(2\omega) \propto \chi_{ijk} E_j(\omega) E_k(\omega) \]

**α structures:** SHG for \( k||z \) allowed

- \( \alpha_x (\varphi = 0^\circ) \): \( \chi_{xxx} = 0 \), \( \chi_{yyy} \neq 0 \)
- \( \alpha_y (\varphi = 90^\circ) \): \( \chi_{xxx} \neq 0 \), \( \chi_{yyy} = 0 \)
- \( \alpha_\rho (\varphi = 0-90^\circ) \): \( \chi_{xxx} \propto \sin \varphi \), \( \chi_{yyy} \propto \cos \varphi \)

**β structures:** SHG for \( k||z \) not allowed

- \( \beta_x, \beta_y, \beta_\rho \): \( \chi_{xxx} = 0 \), \( \chi_{yyy} = 0 \)

Determine \( \beta \) struct. from \( \alpha-\beta \) transition

- \( \alpha_x \rightarrow \beta_y \): \( \chi_{xxx} = 0 \), \( \chi_{yyy} \propto \cos \varphi \)
- \( \alpha_y \rightarrow \beta_x \): \( \chi_{xxx} \propto \sin \varphi \), \( \chi_{yyy} = 0 \)

Polarization of ingoing and outgoing light reveals the magnetic symmetry
SHG Spectrum and Magnetic Symmetry

\[ \propto |\chi_{yyy}|^2 \]
\[ \propto |\chi_{xxx}|^2 \]